

(11) (A) No. 1 130 988

(45) ISSUED 820907

(52) CLASS 23-364  
C.R. CL. 99-172;  
31-1.10

(51) INT. CL. <sup>3</sup>  
A23N 1/00; A23L 1/20; A24B 15/24

(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS FOR EXTRACTIVE TREATMENT OF  
VEGETABLE AND ANIMAL SUBSTANCES

(72) Kurzhals, Hans-Albert;  
Hubert, Peter,  
Germany (Federal Republic of)

(73) Granted to HAG Aktiengesellschaft  
Germany (Federal Republic of)

(21) APPLICATION No. 337,471

(22) FILED 791012

(30) PRIORITY DATE Germany (Federal Republic of)  
(P 28 44 781.6) 781013

No. OF CLAIMS 14

PROCESS FOR EXTRACTIVE TREATMENT OF VEGETABLE  
AND ANIMAL SUBSTANCES

---

ABSTRACT OF THE DISCLOSURE

A process for extractive treatment of vegetable and animal material with a non-reactive solvent mixture having two components, the first of which is gaseous and the second of which has physical properties such that, at the employed temperature, it forms a liquid when mixed with the first component.

BRIEF SUMMARY OF THE INVENTION

The invention relates to a process for the careful extractive treatment of vegetable and animal material with a non-reactive, liquid solvent mixture with adjustable solvent properties without residue problems, either the plant or animal carrier substance or the extracted substances being able to be recovered in a simple manner.

BACKGROUND OF THE INVENTION

Most prior art processes for the extractive treatment of materials of vegetable or animal origin work with solvents consisting of pure substances or mixtures of substances whose components are liquid under normal conditions. Normally, in addition to water, organic solvents are predominantly used, e.g., hydrocarbons, alcohols, acids, esters, ketones, etc., their halogenated derivatives are also frequently being used. In most cases, it is necessary to remove the solvents from the treated materials and/or extracts.

The principal drawback of these solvents is the relatively large intermolecular forces which make it necessary to use large amounts of energy or complicated and extravagant processes for the removal of the solvents. Apart from the economic disadvantage, this often results in changes in the treated material and/or in the extract

having their cause in (chemical) adduct formations, e.g., with the solvent, or in thermal denaturations. This generally renders a complete residue-free removal of the solvent from material and/or extract impossible. Such residues are undesirable.

Many of the solvents used for the extraction of vegetable and animal materials are combustible and thus cause problems in industrial use.

In order to avoid the above-described disadvantages resulting from the use of solvents which are liquid under normal conditions, it has recently been proposed to use processes involving the use of supercritical or liquid gases at high pressures. The adaptation of the solvent properties is mainly by selection of pressure and temperature in the case of supercritical gases and mainly by pressure in the case of liquid gases. Examples of such processes are the recovery of spice extracts (German Patent No. 21 27 611), production of hop extracts (German Patent No. 21 27 618), denicotinization of tobacco (German Patent No. 21 42 205) and production of cocoa butter (German Patent No. 21 27 643).

These processes all require relatively high pressures, generally in excess of 150 bar, for the attainment of sufficiently high degrees of extraction.

BRIEF INTRODUCTION TO THE DRAWINGS

Figures 1 and 2 are schematic diagrams of apparatus suitable for carrying out the process according to the present invention.

DESCRIPTION OF PREFERRED EMBODIMENT

It is an object of the present invention to overcome the above-mentioned disadvantages of the prior art processes. This object is attained by use of a solvent mixture comprising two components,

- a) the first of which is gaseous per se under the employed conditions, and
- b) the second of which in itself has physical properties such that the mixture of (a) and (b) is liquid at the employed temperature.

It has been determined that, optimal adjustment of the solvent properties (selectivity, solubility and yield) is possible by suitable selection of the components of the mixture to be used according to the invention without the above-mentioned disadvantages occurring.

For the first component, which is gaseous per se under the employed conditions, gases are suitable which are not injurious to health, especially non-combustible gases. Gases which occur naturally in the material to be

treated are preferred, and these can be used alone or in mixtures.

The following gases are among those suitable for the first component:  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , (here the decomposition ranges must be considered),  $\text{SF}_6$ , Xe,  $\text{CF}_4$ , methane, ethylene, acetylene, cyclopropane.

For the second component, which in itself has physical properties such that its mixture with the component which is gaseous per se under the employed conditions is liquid at the employed temperature, substances are suitable which are not injurious to health, particularly component substances of the materials to be extracted. This use of component substances as the second component has the advantage that they do not raise food-related legal problems since they are not considered substances in the sense of regulations relating to additives. The following groups of compounds, which are also naturally contained in the starting materials mentioned by way of example, are among those suitable as the second component: hydrocarbons, alcohols, ketones, keto alcohols, acetals, ethers, esters, carboxylic acids, amines, lipids.

Examples of uses for which the process according to the invention is suitable include recovery of:

aroma      oil from roast coffee

tea aroma from black tea

hop extracts

spice extracts having a natural  
composition

tobacco with no or reduced nicotine,

also having reduced condensate content  
vegetable fats and oils

fat-free enzymes

odorous and odoriferous substances from  
vegetable and animal materials

drug extracts

aglycones from glycosides, if appropriate  
after prior cleavage

extracts from citrus fruits

dyestuffs from vegetable materials

vegetable insecticides

meat aromas

animal fats or fat-reduced meat

In many applications of the process of the invention to the starting materials noted above by way of example, all those components are to be completely extracted which in their entirety constitute the valuable substance, and are free of ballast material to the major extent. The selection of the second component must hence be made from the aspect of the separation of a generally complex mixture, in many cases not only one of the above-noted compounds but a mixture of several compounds

being advantageous as the second component. Its selection and concentration in the solvent according to the invention depends (given the criterion of the highest possible solubility for the extract to be recovered) on the nature of the material to be extracted, the selected operating conditions, and the properties of the first component with which a liquid solution is to be obtained.

The temperature of the extraction according to the invention is preferably in the range of about 260 to 400 K, and, if  $\text{CO}_2$  is used as the first component, preferably between room temperature and about 340 K. The extraction pressure is to be at least high enough so that the solution to be selected according to the invention is liquid at the selected composition and adjusted temperature, the upper limit of the extraction pressure to be employed depending merely on commercial considerations.

Surprisingly, in many systems, isothermal pressure increases are accompanied by increases in the velocity of extraction, even though the increase in density of the liquid solution is relatively slight. Conversely, the use of lower pressures makes it possible to reduce the apparatus expenditure.

The quantitative ratio of liquid solution to the material to be extracted should be sufficiently high for



1130988

the duration of extraction to be as short as possible, while on the other hand commercially excessive amounts of solvent should be avoided.

Extraction proceeds in the conventional manner, and can be carried out according to all known processes of solid-liquid extraction, both continuous and batch processes being employable.

Separation of the extract from the solvent is preferably by distillation, by utilizing a miscibility gap of the solvent consisting of the two components, or by shifting the solvent characteristics of the solvent in the single-phase system (e.g., precipitation). In all cases, a pressure and/or temperature change is required. Where a miscibility gap is used, it is particularly advantageous for one of the segregated components to have a significantly better solvent capacity for the extract than the other component. This phase is then discharged from the system, separated by separation processes known per se, and the pure component reintroduced into the system.

Further alternatives for separation of the extract consist of removing the extract by adsorption (bonding to solid substances) or by liquid-liquid extraction from the solvent mixture to be used according to the invention. This type of separation is particularly advantageous where the

1130988

extract is to be utilized further bonded to a solid or liquid carrier material rather than in its pure form.

After extraction is completed, the liquid solution is separated from the material which has been extracted. If this separation occurs while the pressure is simultaneously lowered, substantially only a small portion of the second component remains in the system, and hence in the extracted material, and can if necessary be removed by evacuation, heating, steaming or rinsing with the first component or other inert gases.

Surprisingly, it has been found that, when treating extraction material having a solid matrix, the residues of the two components after separation of the solution are located almost exclusively on the surface of the extraction material, and can thus be removed simply and completely.

In the case of isobaric separation of the solution, the volume it occupies in the extracting system can be replaced by inert gases or by the pure first component. If use is made of inert gases or of first components which are incombustible and which do not support combustion, this method of separation offers the advantage that combustible second components are present in such low concentration during the subsequent evacuation of the apparatus that their mixture with air

1130988

is not ignitable. The described manner of isobaric separation of the solution normally requires no supplemental treatment for the removal of solvent residues.

EXAMPLE I

2.5 kg of air-dry Hallertau hops were extracted in apparatus according to Figure 1 under the following conditions with a liquid mixture of 94 moles %  $\text{CO}_2$  (from supply container VI) and 6 Mol % n-butane (from supply container V2) having a critical temperature of 310.9 K and a critical pressure of 71.9 bar:

extraction pressure: 82.7 bar

extraction temperature: 308.2 K

The solvent was conveyed with the aid of pump P1 and was brought to temperature by heat exchanger W1, circulated through extraction container A and enriched with extract. The pressure of a secondary stream was reduced to 50 bar in separation container B. A butane-rich, liquid phase resulted, containing both dissolved and undissolved extract components, as well as a  $\text{CO}_2$ -rich, gaseous phase, which was almost free of dissolved hop constituents. The latter was withdrawn upwardly out of the separation container. The liquid phase was clarified in separator S, the undissolved extract portion I being obtained. The clarified liquid phase was freed in the distillation apparatus D of

the dissolved hop substances which were obtained as extract portion II. The CO<sub>2</sub>-rich gaseous phase from B was repressurized by compressor P2 and the distillate from D was conveyed by pump P3, and the two material streams were brought together. The resulting mixture, which at this point again had the same composition as the pure solvent, was brought to temperature extraction conditions in heat exchanger W2 and then returned to the main stream in liquid form.

The apparatus according to Figure 1 was operated for four hours. A yield of 355g light green extract was obtained. It was found that extract portion II was particularly rich in such components which are attributable to hop oil, while extract portion I contained relatively few hop oils, but more soft resin proportions.

The following table shows the analytical data for the hops used as starting material, the extract, i.e., the sum of portions I and II, as well as the data for the spent hop grains:

Results of Hop Analysis

<u>Determination of</u>	<u>Untreated Hops</u>	<u>Spent Residue</u>	<u>Extract I + II</u>
% Water	10.5	12.3	3.4
% <u>Total resin</u>	23.0	4.1	91.9
% <u>Soft resin</u>	20.8	2.0	89.4

Results of Hop Analysis (Cont'd)

<u>Provision of</u>	<u>Untreated Hops</u>	<u>Spent Residue</u>	<u>Extract I and II</u>
% $\alpha$ -acids	10.1	< 0.1	46.3
% $\beta$ -acids	10.7	1.9	41.5
% <u>hard resins</u>	2.2	2.3	2.1
% hop oils	1.0	< 0.1	4.9
% tanning materials	4.3	5.3	0

EXAMPLE II

5 kg of ground black pepper with a piperine content of 9.8% were extracted in the apparatus according to Figure 1 with a mixture of 58.8 mole % CO<sub>2</sub> and 41.2 mole % propane at 325 K and 78 bar. The mode of operation was the same as described in Example I. However, separator S was not needed. Rather was the liquid phase which appeared in separation container B after pressure reduction to 45 bar conveyed directly to distillation apparatus D together with the precipitated extract components.

The apparatus was operated for two hours. 936 g of a yellow pepper extract having an intensive odor were obtained containing 51.3% piperine. This corresponds to a yield of 18.7%. The degree of extraction, with respect to piperine, is thus 98%.

The following examples relate to the treatment of tobacco, the aim being the recovery of the vegetable

matrix, and such treatment can proceed in one or more steps.

EXAMPLE III

5 kg of Burley cut tobacco containing 3.7% nicotine in the dry material, were moistened to a water content of 20% and then denicotinized for 2.5 hours in the apparatus shown in Figure 2. The solvent was a liquid mixture consisting of 93 mole % CO<sub>2</sub> (from supply container VI) as the first component and 7 mole % ethanol (from supply container V2, supplied by pump P2) as the second component. The solvent was circulated by means of pump P1 through the tobacco-containing extraction container A and the adsorber C. The latter contained an ion exchange resin as a selectively-acting adsorbent for nicotine. Heat exchanger W served for setting the 316 K extraction temperature. The circulation pressure was 100 bar.

After treatment, the tobacco was re-dried to its initial moisture content of about 10%. The nicotine content in the dry material was 0.03%. Its bulk density had diminished from 170 to 136 kg/m<sup>3</sup>. Otherwise the typical appearance of the cut tobacco was unchanged. The material also had excellent smoking properties with respect to aroma. The condensate content of the treated vis-a-vis the untreated tobacco was reduced by 43%.

EXAMPLE V

The following multi-step process was used for a more aroma-sensitive Virginia tobacco:

First step: The aroma was removed from 5 kg of dry Virginia tobacco having a moisture content of 8% in an apparatus according to Figure 1 and the tobacco conveyed to a previously nicotine-reduced tobacco charge. The starting material was located in extraction container A, and the tobacco to be aromatized in separation container B. The solvent was a liquid mixture consisting of 94 mole % CO<sub>2</sub> and 6 mole % n-butane. The extraction pressure was 88 bar, and the extraction temperature 309 K. The pressure of the aroma-containing solvent stream was reduced in container B with a pressure of 28 bar being set. This resulted in a butane-rich liquid phase and a CO<sub>2</sub>-rich vapor phase, which was withdrawn from B. The liquid phase percolated through the tobacco and thereby gave up most of the aroma substances to the tobacco. It was then withdrawn with the aid of pump P3, but without use of separator S and distillation apparatus D; combined with the CO<sub>2</sub>-rich phase, which had been re-pressurized by pump P2, and recycled to the extraction via heat exchanger W2.

Second Step: The de-aromatized tobacco was then moistened to a water content of 22% and its nicotine content reduced as described in Example III. After

re-drying to about 10%, it was subjected to an aroma transfer from a fresh tobacco charge in container B, as described in the first step. The resulting product had the same appearance as the starting material and very good smoking properties.

Analysis Data

	Starting tobacco	De-aromatized	Nicotine reduced	Re-aromatized
10 % nicotine in dry substance	1.85	1.83	0.04	0.05
bulk density (Kg/m <sup>3</sup> )	170	not determined	not determined	128

EXAMPLE V

25 kg of ground soybeans were extracted in an apparatus according to Figure 1. A solvent consisting of a liquid mixture of 92 mole % CO<sub>2</sub> and 8 mole % pentane was used, with an extraction pressure of 100 bar and an extraction temperature of 339 K. After reducing the pressure to 42 bar, the resulting CO<sub>2</sub>-rich, extract-free gas phase B was repressurized by pump P2. The pentane-rich, extract-containing liquid phase was withdrawn from separation container B and freed of pentane and CO<sub>2</sub> in distillation apparatus D without use of the separator. The distillate was recycled as described in the preceding examples. 4.6 kg of light yellow soy oil was



1130988

obtained. The starting material had a fat content of 18.5% while the residual fat content of the extracted material was  $<0.1\%$ .

EXAMPLE V

500 kg ground, naturally moist orange peels were extracted for the recovery of the inherent coloring matter (carotin) in an apparatus according to Figure 1 with a liquid mixture consisting of 92 mole %  $\text{CO}_2$  and 8 mole % acetone, at an extraction pressure of 90 bar and an extraction temperature of 310 K for 0.5 hours. The separation pressure in container B was 25 bar. The gaseous, extract-free  $\text{CO}_2$ -rich phase was repressurized by pump P2, while the liquid phase was freed of acetone and  $\text{CO}_2$  in distillation apparatus D without use of separator S. The distillate was recycled (see preceding examples). A dark-red oil with a total carotin content of 150 g carotin was obtained.

The carotin content of the starting material was about 320 mg/kg dry material. The yield was thus 93.8%. A residual acetone content of  $<10$  ppm was found in the extract.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Process for the extractive treatment of vegetable and animal matter with a liquid solvent solution which is not injurious to health, and which comprises using a two-component solvent solution
  - a) the first component of which is gaseous per se under the employed conditions, and
  - b) the second component of which has in itself physical properties such that the mixture of the two components is liquid at the employed temperature.
2. Process according to claim 1, wherein the first component is selected from the group comprising CO<sub>2</sub> alone, and gases and gas mixture not injurious to health.
3. Process according to claim 1 or 2, wherein said second component is selected from the group comprising constituents of vegetable or animal matter, and food substances.
4. Process according to claim 1, wherein the operative temperature range is 260 to 400 K.
5. Process according to claim 1, wherein the preferred operating temperature range is room temperature to 340 K.
6. Process according to claim 1, wherein the solvent is circulated and the extract is separated by lowering

the pressure and/or raising the temperature, thereby producing phase separation of the solvent into a gaseous and liquid phase.

7. Process according to claim 6, wherein the extract is removed from the system with the liquid phase, and is then separated from the liquid phase, the latter being recycled.

8. Process according to claim 7, wherein the extract is fractionated by separating a constituent of the extract which is insoluble in the liquid phase prior to recovery of the entire extract from the liquid phase.

9. Process according to claim 8, wherein the extract is separated into more than two fractions by separating the phases in several pressure and/or temperature stages and separately removing the respective undissolved portion of the extract from the particular stage.

10. Process according to claim 1, wherein the extract is bonded to solid adsorbents by adsorption from the solvent.

11. Process according to claim 1, wherein the extract is removed from the solvent by liquid-liquid extraction.

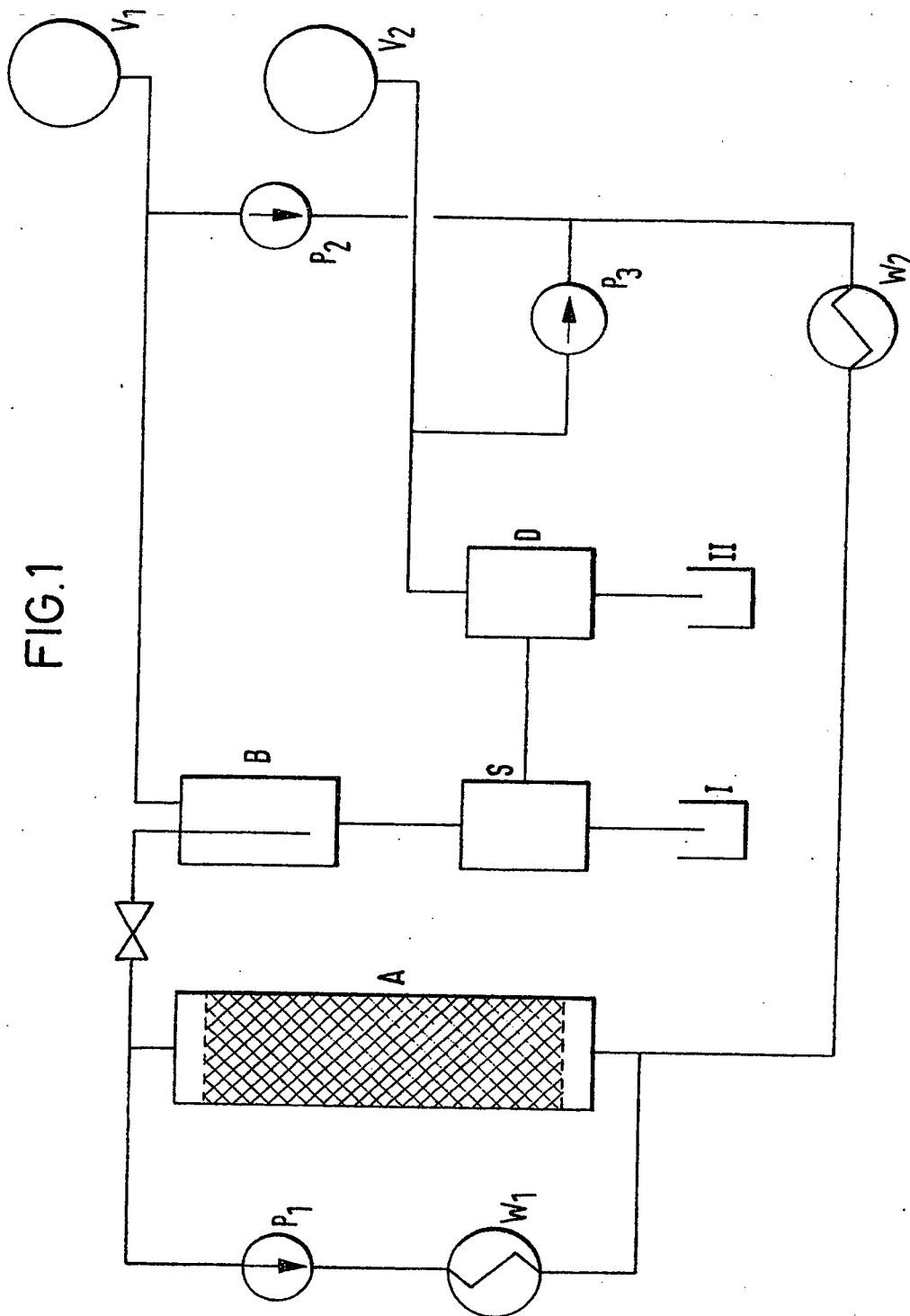
12. Process according to claim 1, wherein the solvent is after the extraction separated from the vegetable or

or animal matter with simultaneous lowering of pressure, and the residual solvent is removed by evacuation, heating, steaming or rinsing with said first, gaseous component or other inert gases.

13. Process according to claim 1, wherein the solvent is removed isobarically from the extraction system after extraction, and that the volume it occupied is replaced by inert gases or by the pure liquid first component in the case of simultaneous lowering of the temperature.

14. Process according to claim 1, wherein the solvent used for extraction contains combustible constituents, and the mixing proportions are such that the mixture is not ignitable in air.





Goudreau, Gage - Dubuc

FIG. 2

